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               LINEAR THERMOMECHANICAL COUPLING EFFECT IN TRANSIENT DEFORMATIN--ETC(U)
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# LINEAR THERMOMECHANICAL COUPLING EFFECT IN TRANSIENT DEFORMATION

STANFORD UNIVERSITY
CALIFORNIA

AUGUST 1976

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|---|
| **1. REPORT NUMBER** <br> Contract No. 25 | **2. GOVT ACCESSION NO.** | **3. RECIPIENT'S CATALOG NUMBER** |
| **4. TITLE (and Subtitle)** <br> LINEAR THERMOMECHANICAL COUPLING EFFECT IN TRANSIENT DEFORMATION | | **5. TYPE OF REPORT & PERIOD COVERED** <br> Technical Interim |
| | | **6. PERFORMING ORG. REPORT NUMBER** <br> SUDAM No. 75-10 |
| **7. AUTHOR(s)** <br> RICHARD W. YOUNG | | **8. CONTRACT OR GRANT NUMBER(s)** <br> N00014-75-C-0698 |
| **9. PERFORMING ORGANIZATION NAME AND ADDRESS** <br> Stanford University <br> Department of Applied Mechanics <br> Stanford, California  94305 | | **10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS** <br> NR 064-471 |
| **11. CONTROLLING OFFICE NAME AND ADDRESS** <br> Office of Naval Research <br> Department of the Navy <br> Washington, D. C.  20025 | | **12. REPORT DATE** <br> August 1976 |
| | | **13. NUMBER OF PAGES** <br> 42 |
| **14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)** | | **15. SECURITY CLASS. (of this report)** <br> UNCLASSIFIED |
| | | **15a. DECLASSIFICATION/DOWNGRADING SCHEDULE** |

**16. DISTRIBUTION STATEMENT (of this Report)**

Approved for public release; distribution unlimited.

**17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)**

Same as above.

**18. SUPPLEMENTARY NOTES**

- 0 -

**19. KEY WORDS (Continue on reverse side if necessary and identify by block number)**

| | |
|---|---|
| Thermomechanical coupling | Irreversible thermodynamics |
| Elasticity | Non-oscillatory deformation |
| Finite elasticity | |
| Viscoelasticity | |

**20. ABSTRACT (Continue on reverse side if necessary and identify by block number)**

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LINEAR THERMOMECHANICAL COUPLING EFFECTS

IN TRANSIENT DEFORMATION[*]

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# ABSTRACT

The interaction between the mechanical deformation and the thermal state of solids is studied. Principles of classical thermodynamics are used to calculate temperature changes arising from the isentropic deformation of elastic solids. The theory of irreversible thermodynamics is used to predict temperature changes due to the adiabatic deformation of viscoelastic solids.

It is found that such temperature changes are small and that the effect of thermomechanical coupling may usually be neglected in the non-oscillatory deformation of linear elastic, finite (rubber) elastic, and linear viscoelastic solids. Data are presented for several metals, rubbers, and plastics.

## INTRODUCTION

In the analysis of mechanical deformation, thermal effects are
usually not considered beyond the occasional noting of the temperature
of the material at the onset of testing. Because the mechanical prop-
erties of the material can be essentially independent of the temperature
over large temperature ranges, this approximation is usually justifiable.
Even when the material properties exhibit significant thermal depen-
dence, the deformation process can cause such a small change in tempera-
ture that its effects may be ignored.

There are some cases, however, especially in the realm of visco-
elastic materials, in which the temperature change and the ensuing
variation of mechanical properties can be important.

We shall concern ourselves with essentially static loadings, such
as simple extension, shear, or bulk compression of solids. These
"static" processes will be referred to as transient. Changes in the
temperature of a body which result from its deformation under such
loadings will be calculated. Knowledge of the effect of temperature
upon the mechanical properties then enables us to gauge the importance
of thermomechanical coupling in a given problem.

The following chapters will deal with the transient loadings of
linear elastic, rubber elastic, and linear viscoelastic solids. We
will not consider here dynamic processes such as vibration or shock
loading.

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CHAPTER ONE

## LINEAR ELASTIC DEFORMATIONS

The effect of thermomechanical coupling in linear elastic solids
is easily derived from the basic equations of thermodynamics and thermo-
elasticity. Results in this field are already well established (see
for example Nowacki [1] and Biot [2]), and the following derivation is
presented primarily as a basis and as a source of comparison for subse-
quent developments.

In the ensuing equations, quantities such as internal energy, $U$ ,
heat, $Q$ , work, $W$ , entropy, $S$ , et cetera, are measured per unit of
original volume of an infinitesimal body. We write the first law of
thermodynamics as[1]

$$dU = dQ + dW \tag{1}$$

The absolute temperature of the body is denoted by $T$ . From the second
law of thermodynamics, applied to reversible processes, we write:

$$dQ = TdS \tag{2}$$

The work done on the body, per unit of original volume, is expressed by[2]

$$dW = \sigma_{ij}d\epsilon_{ij} \tag{3}$$

---

1  dW is the total increment of work done on (not by) the body, and it
   includes work done by atmospheric pressure and any other pre-loads.
   These are departures from usual thermodynamic convention. dQ denotes
   the increment of heat added to the body.

2  Summation convention will be used, implying summation over repeated
   free indices. Thus
   $$\sigma_{ij}d\epsilon_{ij} = \sum_{i=1}^{3} \sum_{j=1}^{3} \sigma_{ij}d\epsilon_{ij}$$

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where $\sigma_{ij}$ and $\varepsilon_{ij}$ are the conventional stresses and infinitesimal strains of classical elasticity.[3]

Using the definition of the Helmholtz free energy,

$$A = U - TS , \tag{4}$$

entropy may be expressed as a function of temperature and the strain tensor, $S = S(T,\underline{\varepsilon})$ . From eqs. (1-4), we have

$$dA = \sigma_{ij}d\varepsilon_{ij} - SdT \tag{5}$$

Thus:[4]

$$\left.\frac{\partial A}{\partial \varepsilon_{ij}}\right|_{T,\underline{\varepsilon}'} = \sigma_{ij} \qquad , \qquad \left.\frac{\partial A}{\partial T}\right|_{\underline{\varepsilon}} = -S \tag{6a,b}$$

It follows from the commutivity of partial differentiation and the regular behavior of $A$ that

$$\left.\frac{\partial S}{\partial \varepsilon_{ij}}\right|_{T,\underline{\varepsilon}'} = -\left.\frac{\partial \sigma_{ij}}{\partial T}\right|_{\underline{\varepsilon}} \tag{7}$$

From eq. (2) and the definition of heat capacity, we write

---

3  To be precise, these can be interpreted as the second Piola-Kirchoff stress (force per unit of undeformed area) and the Lagrange strain (attributed to Cauchy.) In the infinitesimal case, these measures differ insignificantly from various other common measures. For detailed discussion of these points, see Truesdell and Noll [3] and Rivlin [4].

4  The notation $|_{\underline{\varepsilon}}$ implies that all elements of $\underline{\varepsilon}$ are held fixed with the exception of the one indicated in the partial differential operator.

$$\frac{\partial S}{\partial T}\bigg|_{\underline{\varepsilon}} = \frac{\rho_o C_V}{T} \tag{8}$$

where $\rho_o$ is the material density in the undeformed state and $C_V$ the heat capacity per unit mass at constant volume or, to be more precise, constant strain.

The partial derivative on the right-hand side of eq. (7) may be evaluated directly from consideration of the thermoelastic stress-strain laws. Letting $\mu$ and $\lambda$ denote the isothermal Lamé constants, $\alpha$ the volumetric coefficient of thermal expansion, and $\theta$ the increase in temperature from the strain-free state, strain is given by

$$\varepsilon_{ij} = \frac{1}{2\mu}(\sigma_{ij} - \sigma_{o_{ij}}) - \frac{\lambda}{2\mu(2\mu+3\lambda)}(\sigma_{kk} - \sigma_{o_{kk}})\delta_{ij} + \frac{\alpha}{3}\theta\delta_{ij} \quad , \tag{9}$$

where $\sigma_{o_{ij}}$ is the pre-loading, the loads existing in the strain-free state. The most common example of pre-loading is atmospheric pressure. Inverting these relations, we have

$$\sigma_{ij} = \sigma_{o_{ij}} + 2\mu\varepsilon_{ij} + \lambda\varepsilon_{kk}\delta_{ij} - \alpha K\theta\delta_{ij} \tag{10}$$

where $K = \lambda + \frac{2\mu}{3}$ is the isothermal bulk modulus.

Writing entropy in terms of its partial derivatives, and substituting from eqs. (7), (8), and (10):

$$dS = \frac{\rho_o C_V}{T} dT + \alpha K\delta_{ij}d\varepsilon_{ij} \tag{11}$$

Thermomechanical coupling effects are usually ignored in non-oscillatory situations. An argument often cited in support of this

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approximation is one which we shall refer to here as the "equivalent heat" argument. Stated simply, it states that if one were to supply the thermodynamic system (the infinitesimal body) with an amount of heat equivalent to the mechanical work done on the system, the resulting change in temperature of the system would be an upper bound for the actual change in temperature. (The change in temperature predicted by this argument is denoted by $dT_{eqh}$.) Thus:

$$dW = dQ = \rho_o C_V dT_{eqh} \tag{12}$$

and from eq. (3),

$$dT_{eqh} = \frac{\sigma_{ij} d\varepsilon_{ij}}{\rho_o C_V} \tag{13}$$

$dT_{eqh}$ is compared with the result of the thermodynamic analysis, denoted by $dT_{thm}$. For an adiabatic, reversible process, $dS = 0$ and eq. (11) becomes:

$$dT_{thm} = -\frac{\alpha TK}{\rho_o C_V} \delta_{ij} d\varepsilon_{ij} = -\frac{\alpha TK}{\rho_o C_V} d\varepsilon_{kk} \tag{14}$$

Integrating eqs. (13) and (14), making the approximations that $\alpha$ and $K$ are constant, $C_V$ is linear in temperature, and $\Delta T$ is small with respect to $T$, we find that:

$$\Delta T_{thm} = -\frac{\alpha TK}{\rho_o C_V} \Delta\varepsilon_{kk} \tag{15}$$

and

$$\Delta T_{eqh} = \frac{1}{\rho_o C_V} \ (\sigma_{o_{ij}} + \frac{1}{2} \ \Delta\sigma_{ij})\Delta\varepsilon_{ij} \tag{16}$$

Comparison of eqs. (15) and (16) shows that $\Delta T_{eqh}$ is a poor measure of $\Delta T_{thm}$, the actual temperature change. $\Delta T_{thm}$ is dependent solely upon the volume change and is thus identically zero for any equivo-luminal deformation. $\Delta T_{eqh}$, however, is proportional to the incre-ment in strain energy and is affected by shear deformations. In such cases, $\Delta T_{eqh}$ does indeed serve as an upper bound for the change in temperature, but it is misleading to place an upper bound on a quantity which must be zero.

In the case of hydrostatic compression, $\Delta T_{eqh}$ can fall far short of $\Delta T_{thm}$. As an example, consider the compression of a speci-men by a pressure of n atmospheres. Denoting one atmosphere of pressure by P, then $\sigma_{o_{ij}} = - P\delta_{ij}$, $\Delta\sigma_{ij} = - nP\delta_{ij}$, and $\Delta\varepsilon_{ij} = - nP\delta_{ij}/3K$. Substitution into eqs. (15) and (16) leads to:

$$\frac{\Delta T_{thm}}{\Delta T_{eqh}} = \frac{2\alpha TK}{(2+n)P} \tag{17}$$

The ratio can be quite large, as is seen in the following tabulation:

TABLE 1:[5]                    Sample Values of ($\alpha TK/P$)

   p = 14.7 psi          T = 298°K

| Material | $\alpha$, (°K$^{-1}$) | K, (psi) | $\alpha TK/P$, (--) |
|---|---|---|---|
| mild steel | $3.6 \times 10^{-5}$ | $24.6 \times 10^6$ | $1.8 \times 10^4$ |
| polyisoprene(ebonite rubber) | $1.9 \times 10^{-4}$ | $6.0 \times 10^5$ | $2.3 \times 10^3$ |
| polyethylene(low density) | $7.4 \times 10^{-4}$ | $4.8 \times 10^5$ | $7.2 \times 10^3$ |

---

5   From [5], table 1-59; [6], p. 708;[7], sec VI; [8], table 9.1 .

Even in the case of ebonite, the most favorable case presented, the
ratio of $\Delta T_{thm}$ to $\Delta T_{eqh}$ does not reach unity until the material
is compressed by almost 4600 atmospheres. Pearson [9] presents a
calculation for a cube of steel compressed from an initially unstressed
state. In his example, the ratio of $\Delta T_{thm}$ to $\Delta T_{eqh}$ is unbounded as
the applied pressure approaches zero, as may be seen by examination
of eqs. (15) and (16) with $\sigma_{o_{ij}} = 0$ .

Despite the failure of $\Delta T_{eqh}$ to predict, or even to provide an
upper bound on, the thermal effects of deformation, these effects are
still negligible for infinitesimal elastic deformation, as is later
seen in Chapter Four.

## FINITE ELASTIC DEFORMATIONS

Since many polymers exhibit rubber elasticity, we perform a similar analysis for finite elasticity. We will deal only with principal stresses, and will use extension ratios and true stress (force per unit of deformed area, sometimes called Cauchy stress) defined as follows:[6,7]

$$\lambda_i = L_i/L_{o(i)} = 1 + \varepsilon_{i(i)} \tag{18}$$

$$t_i = f_i/L_j L_k = \sigma_{i(i)}/\lambda_j \lambda_k \quad , \quad i \neq j \neq k \tag{19}$$

In terms of these variables, the first law of thermodynamics becomes, for reversible processes:

$$dU = TdS + (V/V_o)t_i dLn\lambda_i \tag{20}$$

Eq. (5) becomes:

$$dA = (V/V_o)t_i dLn\lambda_i - SdT \tag{21}$$

We proceed as in the infinitesimal case, noting that $V = V_o\lambda_1\lambda_2\lambda_3$, so that constant $\underset{\sim}{\lambda}$ $\left(\underset{\sim}{\lambda} = (\lambda_1, \lambda_2, \lambda_3)^T\right)$ implies constant volume.[8]

---

6 The extension ratio is closely related to the natural, or logarithmic, strain; $\varepsilon_i = Ln\lambda_i$ .

7 Numerical indices and indices hidden in parentheses are not subject to implied summation.

8 T used as a superscript to a vector or a matrix will denote the transpose of that quantity. T used as a scalar will continue to denote absolute temperature.

As in eq. (8),

$$\frac{\partial S}{\partial T}\bigg|_{\underset{\sim}{\lambda}} = \rho_o C_V / T \tag{22}$$

Similarly to eqs. (6),

$$\frac{\partial A}{\partial T}\bigg|_{\underset{\sim}{\lambda}} = - S \qquad , \qquad \frac{\partial A}{\partial \lambda_i}\bigg|_{T, \underset{\sim}{\lambda}'} = \frac{V t_i}{V_o \lambda(i)} \tag{23a,b}$$

Thus:

$$\frac{\partial S}{\partial \lambda_i}\bigg|_{T, \underset{\sim}{\lambda}'} = \frac{-V}{V_o \lambda(i)} \; \frac{\partial t_i}{\partial T}\bigg|_{\underset{\sim}{\lambda}} \tag{24}$$

From eqs. (22) and (24) we have

$$dS = \frac{\rho_o C_V}{T} \, dT - \frac{V}{V_o \lambda(i)} \; \frac{\partial t_i}{\partial T}\bigg|_{\underset{\sim}{\lambda}} d\lambda_i \tag{25}$$

For an isentropic process, we have

$$dT_{thm} = \frac{VT}{\rho_o V_o C_V \lambda(i)} \; \frac{\partial t_i}{\partial T}\bigg|_{\underset{\sim}{\lambda}} d\lambda_i \; , \tag{26}$$

whereas the equivalent heat argument gives

$$dT_{eqh} = dW/\rho_o C_V = \frac{V}{V_o \rho_o C_V} \; \frac{t_i}{\lambda(i)} \, d\lambda_i \tag{27}$$

Integrating eqs. (26) and (27),

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$$\Delta T_{thm} = \frac{T_o}{\rho_o V_o C_V} \int \frac{V}{\lambda_{(i)}} \left. \frac{\partial t_i}{\partial T} \right|_{\underset{\sim}{\lambda}} d\lambda_i \tag{28}$$

$$\Delta T_{eqh} = \frac{1}{\rho_o V_o C_V} \int \frac{V}{\lambda_{(i)}} t_i d\lambda_i \tag{29}$$

At this point we consider possible forms of the function $t_i = t_i(\underset{\sim}{\lambda}, T)$. In most references, it is assumed that stress varies as a linear function of temperature in strain control experiments. This assumption is well verified by experimental results (Meyer and Ferri [10] and Anthony, Caston, and Guth [11] as cited in Treloar [12]). As a further motivation, we shall show that this linear dependence is a direct result of another physical observation, that the heat capacity at constant volume is independent of the deformational state over large ranges of deformation, that is to say,

$$C_V(\underset{\sim}{\lambda}, T) = C_V(T) \tag{30}$$

Taking eqs. (22) and (24) and invoking the commutivity of partial differentiation, derivation of the second partial derivate of S with respect to $\lambda_i$ and T requires that

$$\frac{\rho_o}{T} \left. \frac{\partial C_V}{\partial \lambda_i} \right|_{T,\underset{\sim}{\lambda}} = \frac{-V}{V_o \lambda_{(i)}} \left. \frac{\partial^2 t_i}{\partial T^2} \right|_{\underset{\sim}{\lambda}} \tag{31}$$

Eq. (31) and the form of eq. (30) require that

$$\left. \frac{\partial^2 t_i}{\partial T^2} \right|_{\underset{\sim}{\lambda}} = 0 \tag{32}$$

which, integrated twice, becomes:

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$$t_i(\underset{\sim}{\lambda}, T) = h_i(\underset{\sim}{\lambda})T + g_i(\underset{\sim}{\lambda}) \tag{33}$$

Conversely, assumption of eq. (33) leads to eq. (30). Using the form of eq. (33), eqs. (28) and (29) become:

$$\Delta T_{thm} = \frac{T_o}{\rho_o V_o C_V} \int \frac{V}{\lambda_{(i)}} \, h_i(\underset{\sim}{\lambda}) d\lambda_i \tag{34}$$

$$\Delta T_{eqh} = \Delta T_{thm} + \frac{1}{\rho_o V_o C_V} \int \frac{V}{\lambda_{(i)}} g_i(\underset{\sim}{\lambda}) \, d\lambda_i \tag{35}$$

As a sample calculation using eqs. (34) and (35), we consider the uniaxial extension of natural rubber and use data given in Treloar [12]. Using the simple extension law for a Mooney material and the form of Eq. (33) as guides, the data presented may be reasonably well fitted by:

$$t(\lambda, T) = [.01(\lambda^2 - \lambda^{-1}) - .001] \, T + 1.7(\lambda - \lambda^{-2}) + 0.4 \ (Kg/cm^2) \tag{36}$$

Letting $V = V_o$ and $T = 300°K$, tables of $\rho_o C_V \Delta T_{thm}$ and $\rho_o C_V (\Delta T_{eqh} - \Delta T_{thm})$ are presented.

TABLE 2a: $\rho_o C_V \Delta T_{thm}$  TABLE 2b: $\rho_o C_V (\Delta T_{eqh} - \Delta T_{thm})$

| $\lambda$ \ $\Delta\lambda$ | .001 | .01 | .1 | 1. | $\lambda$ \ $\Delta\lambda$ | .001 | .01 | .1 | 1. |
|---|---|---|---|---|---|---|---|---|---|
| 1.0 | * | * | .014 | 2.8 | 1.0 | * | * | .061 | 1.3 |
| 1.1 | .00055 | .0058 | .092 | 3.2 | 1.1 | .00078 | .0080 | .093 | 1.4 |
| 1.2 | .0013 | .013 | .16 | 3.9 | 1.2 | .00105 | .0106 | .115 | 1.5 |
| 1.5 | .0030 | .030 | .32 | 5.0 | 1.5 | .0015 | .015 | .15 | 1.7 |
| 2.0 | .0051 | .051 | .53 | 6.9 | 2.0 | .0017 | .017 | .17 | 1.7 |
| 3.0 | .0086 | .087 | .87 | 10.2 | 3.0 | .0018 | .018 | .18 | 1.8 |

(table values in $Kg/cm^2$)

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No calculations are made at points marked with (*) because the results would be far too sensitive to the constants chosen in eq. (36) to be meaningful.

In the case of uniaxial extension, $\Delta T_{eqh}$ consistently overestimates the temperature rise. This overestimation varies from around 20% to over 400% in the examples calculated, and is seen to be more reasonable for higher initial and subsequent extensions. Again, the actual temperature rise is seen to be negligible. For the most extreme case shown, extension of a specimen from $\lambda = 3$ to $\lambda = 4$, thermodynamics predicts an increase of 0.65°C ($\Delta T_{eqh}$ is 0.76°C.) In rubber elasticity, such effects may be ignored.

CHAPTER THREE

## LINEAR VISCOELASTIC DEFORMATIONS

The thermodynamic analysis of viscoelastic materials is far more complicated than that of elastic media. In the viscoelastic case, stress and strain are no longer simple functions of each other, but can instead be related through differential operators or through more general functionals. Furthermore, deformation processes are irreversible. Comprehensive discussion of these problems may be found in several texts, and reference is made here to Flügge [13], Lee [14], and Christensen [15].

In this work, we shall deal with stress-strain relations in the form of hereditary integrals over the entire previous history of the material. We shall restrict ourselves to consideration of viscoelastic materials which can be described as linear in the sense that a Boltzmann superposition may be employed for complicated or continuously varying stress or strain histories. Discussion of this technique may be found in references [13-15], and further comments, including some examples of limitations and exceptions to this linearity, are available in Staverman and Schwarzl [16], Leaderman [17], and Matsuoka, Aloisio, and Blair [18].

Further complication is introduced by the fact that viscoelastic material properties exhibit marked temperature dependence. Polymer chemists have long noted this behavior and have searched for good macroscopic descriptions as well as microscopic explanations for the phenomena. Ferry [19] and Tobolsky, in conjunction with several co-workers [20-23], provide many data showing a particular relationship between the temperature and the time history of mechanical deformations. Schwarzl and

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Staverman [24] discuss the physics of this relationship and provide the term "thermorheologically simple" to denote the class of materials exhibiting it. Morland and Lee [25] have generalized the time-temperature relationship to include the effects of continuously varying temperature history. Many polymers can be modeled as thermorheologically simple. This work, however, deals with small temperature excursions from the equilibrium state, and the question of thermorheological simplicity need not be considered.

Rivlin [26] and Green and Rivlin [27] use functionals to express viscoelastic mechanical properties and they examine the form which these functionals may assume. Coleman [28] applies this procedure to the remaining thermodynamic variables. The same approach is developed in a more phenomenological manner by Hunter [29], Pipkin [30], Breuer and Onat [31], Christensen and Naghdi [32], and Cost [33]. In their work, material laws are expressed in single and multiple integral form.

The dissipation inherent in viscoelasticity necessitates the consideration of non-equilibrium, irreversible thermodynamics. Two of the classical texts in this field, providing reference to the pioneering efforts and discussion of the basic principles involved, are those of De Groot [34] and Prigogine [35].

In the application of irreversible thermodynamics to viscoelasticity, Biot [36,37] expresses entropy in "near-equilibrium" states as a quadratic expansion in an indefinitely large number of "hidden coordinates" and proceeds to derive stress-strain laws analogous to spring-dashpot models of viscoelasticity. Eringen [38] and Schapery [39] apply this procedure to several problems in continuum mechanics.

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In 1966, Valanis [40] published a paper showing that solutions to the equations resulting from the hidden variable approach may be expressed as integral operators of the form employed in the phenomenological approach.

In this chapter, thermodynamical equations will be formulated in terms of hidden coordinates, as in reference [39], and will be solved in the manner suggested by Valanis [40]. The solutions will then be used to prove an important symmetry property; this, in turn, will enable us to apply the results to the question of thermomechanical coupling effects.

Keeping our previous notation for entropy, internal energy (both per unit original volume), and temperature, we now denote stress and strain by six-element column vectors, $\underset{\sim}{\sigma}$ and $\underset{\sim}{q}_1$ , respectively, such that $dW = \underset{\sim}{\sigma}^T d\underset{\sim}{q}_1$ . A column vector of "hidden variables," $\underset{\sim}{q}_2$ , is defined as the vector whose elements consist of all the variables necessary to complete the definition of the thermodynamic state. The unknown number of elements of $\underset{\sim}{q}_2$ will be denoted by $N$ . As before, our thermodynamic system is an infinitesimal, homogeneous body having uniform temperature.

In the manner of De Groot [34], we define the quantity $dS_I$ , the internal entropy production, by:

$$dS_I = dS - dQ/T \tag{37}$$

We express the entropy as a function of the state variables, $U$ , $\underset{\sim}{q}_1$ , and $\underset{\sim}{q}_2$ , and introduce the convenient notation:

$$\underset{\sim}{^1\partial S} = \left.\frac{\partial S}{\partial \underset{\sim}{q}_1}\right|_{U,\underset{\sim}{q}_1',\underset{\sim}{q}_2} \qquad , \qquad \underset{\sim}{^2\partial S} = \left.\frac{\partial S}{\partial \underset{\sim}{q}_2}\right|_{U,\underset{\sim}{q}_1,\underset{\sim}{q}_2'} \tag{38a,b}$$

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No work can be done if the deformations, $q_1$, are held fixed, and there are no internal irreversibilities associated with processes for which $dq_1 = 0 = dq_2$ (see Schapery [39]). Therefore, from eqs. (1) and (2):

$$\left.\frac{\partial S}{\partial U}\right|_{q_1, q_2} = 1/T \tag{39}$$

From eqs. (38) and (39):

$$TdS = dU + T(^1\partial S)^T dq_1 + T(^2\partial S)^T dq_2 \tag{40}$$

Rewriting eqs. (1) and (37):

$$dU = dQ + \sigma^T dq_1 \tag{41}$$

$$TdS_I = TdS - dQ \tag{42}$$

Summing eqs. (40-42), we have:

$$TdS_I = [\sigma^T + T(^1\partial S)^T] dq_1 + T(^2\partial S)^T dq_2 \tag{43}$$

We define:

$$X_1 = \sigma + T(^1\partial S) \quad , \quad X_2 = T(^2\partial S) \tag{44a,b}$$

and write:

$$TdS_I = X_1^T dq_1 + X_2^T dq_2 \tag{45}$$

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Dividing both sides of eq. (45) by a small time increment, we write:

$$T\dot{S}_I = \underset{\sim}{X}_1^T \dot{\underset{\sim}{q}}_1 + \underset{\sim}{X}_2^T \dot{\underset{\sim}{q}}_2 \tag{46}$$

where a superposed dot denotes differentiation with respect to time or, as later used under an integral, with respect to the time-like argument.

We now seek more information about the function $\dot{S}_I$. The coefficients, $\underset{\sim}{X}_1^T$ and $\underset{\sim}{X}_2^T$, in eq. (46) can depend upon the state variables, $T$, $\underset{\sim}{q}_1$, and $\underset{\sim}{q}_2$, and, additionally, upon the applied stresses, $\underset{\sim}{\sigma}$. If we postulate a relationship between these quantities and the rates of change of the system, $\dot{\underset{\sim}{q}}_1$, $\dot{\underset{\sim}{q}}_2$, and $\dot{\theta}$, we can write $\dot{S}_I$ as a function of these latter variables directly. Accordingly, we shall expand $\dot{S}_I$ in a truncated Taylor series about an equilibrium state (in which $\dot{\theta} = 0$, $\dot{\underset{\sim}{q}}_1 = \underset{\sim}{0} = \dot{\underset{\sim}{q}}_2$), neglecting all terms of higher than second order.

$$\dot{S}_I = \alpha_o + \underset{\sim}{\alpha}_1^T \dot{\underset{\sim}{q}}_1 + \underset{\sim}{\alpha}_2^T \dot{\underset{\sim}{q}}_2 + \alpha_3 \dot{\theta} + \frac{1}{2}\dot{\underset{\sim}{q}}_1^T(\beta_1 \dot{\underset{\sim}{q}}_1 + \beta_2 \dot{\underset{\sim}{q}}_2) +$$

$$+ \frac{1}{2}\dot{\underset{\sim}{q}}_2^T(\beta_2^T \dot{\underset{\sim}{q}}_1 + \beta_3 \dot{\underset{\sim}{q}}_2) + (\dot{\underset{\sim}{q}}_1^T \underset{\sim}{\gamma}_1 + \dot{\underset{\sim}{q}}_2^T \underset{\sim}{\gamma}_2)\dot{\theta} + \frac{1}{2}\gamma_3 \dot{\theta}^2 \tag{47}$$

$\beta_1$, $\beta_2$, and $\beta_3$ are constant matrices, $\beta_1$ and $\beta_3$ being symmetric. This expansion may be simplified by noting that, according to the second law of thermodynamics, $\dot{S}_I = 0$ in an equilibrium state; thus $\alpha_o = 0$. The second law also requires that $\dot{S}_I$ never be negative. Since the $\dot{q}_i$'s and $\dot{\theta}$ may be arbitrarily small and are

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not restricted as to sign, this requires that $\alpha_1 = 0 = \alpha_2$ , that $\alpha_3 = 0$ , and that $\beta_1$ and $\beta_3$ be positive semi-definite. Since the elements of $q_2$ are all associated with internal dissipation, $\beta_3$ must actually be positive definite. Eq. (47) now reduces to

$$\dot{S}_I = \frac{1}{2}[\dot{q}_1^{\ T}(\beta_1\dot{q}_1 + \beta_2\dot{q}_2 + \gamma_1\dot{\theta}) + \dot{q}_2^{\ T}(\beta_2^{\ T}\dot{q}_1 + \beta_3\dot{q}_2 + \gamma_2\dot{\theta}) +$$

$$\tag{48}$$

$$+ (\gamma_1^{\ T}\dot{q}_1 + \gamma_2^{\ T}\dot{q}_2 + \gamma_3\dot{\theta})\dot{\theta}]$$

Comparison with eq. (46) reveals that the three sets of terms in parentheses are the three "irreversible forces" associated with $\dot{q}_1^{\ T}$ , $\dot{q}_2^{\ T}$ , and $\dot{\theta}$ . We note, however, that the third term is zero, since $\dot{\theta}$ does not appear explicitly in eq. (46). This is reasonable since an increase in temperature of the system, if not accompanied by any changes in the mechanical or "hidden" coordinates, does not cause internal dissipation. This further reduces eq. (48) by requiring that $\gamma_3 = 0$ and that $\gamma_1 = 0 = \gamma_2$ . We now write the "irreversible forces" as:

$$X_1 = \frac{1}{2}T_o(\beta_1\dot{q}_1 + \beta_2\dot{q}_2) \tag{49a}$$

$$X_2 = \frac{1}{2}T_o(\beta_2^{\ T}\dot{q}_1 + \beta_3\dot{q}_2) \tag{49b}$$

where $T$ becomes $T_o$ in keeping with the truncation of the power series (eq. (47)) to second order, and solutions for the $X_i$ involving antisymmetric matrices are suppressed in accordance with the symmetry requirements of Onsager's principle [41,42]. It should also be noted that the quadratic terms in eq. (47), resulting from our assumption of

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a relationship between the $\dot{q}_i$'s and $\dot{\theta}$ and the state variables, reflect Onsager's principle of linear relationship between "forces and fluxes." Onsager's principle is restricted to near-equilibrium states; our derivation is also, due to the truncation of the Taylor series after the quadratic terms.

We now introduce the free enthalpy (Gibbs' function):

$$G = U - TS - \sigma_o^T q_1 \tag{50}$$

where $\sigma_o$ is the stress in the unstrained state. Differentiating eq. (50) and substituting from eqs. (41-43):

$$dG = - SdT - [\sigma_o + T(^1\partial S)]^T dq_1 - T(^2\partial S)^T dq_2 \tag{51}$$

so that

$$\left.\frac{\partial G}{\partial q_1}\right|_{T,q_1',q_2} = - [\sigma_o + T(^1\partial S)] \tag{52a}$$

$$\left.\frac{\partial G}{\partial q_2}\right|_{T,q_1,q_2'} = - T(^2\partial S) \quad , \qquad \left.\frac{\partial G}{\partial T}\right|_{q_1,q_2} = - S \tag{52b,c}$$

If the free enthalpy is expanded about an unstrained equilibrium state (in which $\theta = 0$, $q_1 = 0 = q_2$), we obtain:

$$G = G_o + a_3\theta + a_1^T q_1 + a_2^T q_2 - \frac{1}{2}b_3\theta^2 + \frac{1}{2}q_1^T(B_1 q_1 + B_2 q_2) + $$
$$+ \frac{1}{2}q_2^T(B_2^T q_1 + B_3 q_2) + (b_1^T q_1 + b_2^T q_2)\theta \tag{53}$$

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where $B_1$ and $B_3$ are symmetric. It may be shown (see ref. [39]) that $G \geq G_0$ for any nearby states in which $\theta = 0$. Therefore, $\underset{\sim}{a}_1 = \underset{\sim}{0} = \underset{\sim}{a}_2$ and $B_1$ and $B_3$ must be positive semi-definite. Irreversibility further requires that $B_3$ be positive definite. The negative sign is assigned to the $\theta^2$ term for later convenience.

Differentiating eq. (53),

$$\frac{\partial G}{\partial \underset{\sim}{q}_1} = - T(^1\underset{\sim}{\partial} S) - \underset{\sim}{g}_0 = B_1 \underset{\sim}{q}_1 + B_2 \underset{\sim}{q}_2 + \underset{\sim}{b}_1 \theta \tag{54a}$$

$$\frac{\partial G}{\partial \underset{\sim}{q}_2} = - T(^2\underset{\sim}{\partial} S) = B_2^{\ T} \underset{\sim}{q}_1 + B_3 \underset{\sim}{q}_2 + \underset{\sim}{b}_2 \theta \tag{54b}$$

$$\frac{\partial G}{\partial T} = -S = a_3 + \underset{\sim}{b}_1^{\ T} \underset{\sim}{q}_1 + \underset{\sim}{b}_2^{\ T} \underset{\sim}{q}_2 - b_3 \theta \tag{54c}$$

Hence, from eqs. (44), (49), and (54),

$$\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_0 = \frac{1}{2} T_0 (\beta_1 \dot{\underset{\sim}{q}}_1 + \beta_2 \dot{\underset{\sim}{q}}_2) + B_1 \underset{\sim}{q}_1 + B_2 \underset{\sim}{q}_2 + \underset{\sim}{b}_1 \theta \tag{55a}$$

$$\underset{\sim}{0} = \frac{1}{2} T_0 (\beta_2^{\ T} \dot{\underset{\sim}{q}}_1 + \beta_3 \dot{\underset{\sim}{q}}_2) + B_2^{\ T} \underset{\sim}{q}_1 + B_3 \underset{\sim}{q}_2 + \underset{\sim}{b}_2 \theta \tag{55b}$$

We note that $B_3$ and $\beta_3$ may be simultaneously diagonalized by a non-singular matrix, $V$ (see Franklin [43]). Since both matrices are positive definite, we may further require that $V$ be such that

$$V^T B_3 V = \Lambda \quad \text{and} \quad V^T \beta_3 V = I \tag{56a,b}$$

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where $I$ is the $N \times N$ identity matrix and $\Lambda$ is a diagonal matrix of positive constants. If we define the transformation of variables

$$\underset{\sim}{q} = V^{-1}\underset{\sim}{q}_2 \quad , \tag{57}$$

eq. (55b) may be rewritten as

$$\underset{\sim}{0} = \frac{1}{2}T_o\underset{\sim}{\dot{q}} + \frac{1}{2}T_o V^T \beta_2{}^T \underset{\sim}{\dot{q}}_1 + V^T B_2{}^T \underset{\sim}{q}_1 + \Lambda \underset{\sim}{q} + V^T \underset{\sim}{b}_2 \theta \tag{58}$$

Analogous to a result in Valanis [40],

$$\underset{\sim}{q}(t) = -\int_0^t e^{-\frac{2}{T_o}(t-\tau)\Lambda} V^T [\beta_2{}^T \underset{\sim}{\dot{q}}_1(\tau) + \frac{2}{T_o}(B_2{}^T \underset{\sim}{q}_1(\tau) + \underset{\sim}{b}_2 \theta(\tau))]d\tau \tag{59}$$

solves eq. (58). Integration by parts yields a more desirable form of this equation:

$$\underset{\sim}{q} = -\Lambda^{-1}V^T[B_2{}^T \underset{\sim}{q}_1 + \underset{\sim}{b}_2 \theta] - \int_0^t E_x(t-\tau)[V^T\beta_2{}^T - \Lambda^{-1}V^T B_2{}^T]\underset{\sim}{\dot{q}}_1 d\tau + $$
$$+ \int_0^t E_x(t-\tau)\Lambda^{-1}V^T\underset{\sim}{b}_2\dot{\theta}d\tau \tag{60}$$

where:

$$E_x(t-\tau) = e^{-\frac{2}{T_o}(t-\tau)\Lambda} \tag{61}$$

and $E_x$ commutes with $\Lambda$ and $\Lambda^{-1}$.

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The form of eq. (60) is of great significance. We have started with N "hidden coordinates", $q_2$ , where N is an unknown, arbitrarily large number. After rearranging these coordinates in a convenient manner (see eq. (57)), we find that they are simply various complicated expressions of the previous deformation and temperature histories. Thus the current state of the thermodynamic system is prescribed as a functional of the temperature and the physical deformation from the onset of activity to the current time. Furthermore, the fact that the elements of $\Lambda$ are positive shows that this functional is similar to the relaxation modulus, familiar in isothermal viscoelasticity.

Applying eqs. (57), (58), and (60) to eq. (55a), we find that

$$\sigma - \sigma_o = [B_1 - B_2 V \Lambda^{-1} V^T B_2{}^T] q_1 + [b_1 - B_2 V \Lambda^{-1} V^T b_2] \theta +$$

$$+ \frac{1}{2} T_o [\beta_1 - \beta_2 V V^T \beta_2{}^T] \dot{q}_1 +$$

$$+ \int_o^t [B_2 V \Lambda^{-1} - \beta_2 V] E_x(t-\tau) V^T \dot{b}_2 \dot{\theta} d\tau + \tag{62}$$

$$- \int_o^t [B_2 V \Lambda^{-1} - \beta_2 V] E_x(t-\tau) [\Lambda V^T \beta_2{}^T - V^T B_2{}^T] \dot{q}_1 d\tau$$

Referring to eq. (54c) and taking $a_3 = - S \Big|_{equil} \equiv - S_o$ , application of eqs. (57) and (60) yields:

$$S - S_o = [\underset{\sim}{b}_2{}^T V \Lambda^{-1} V^T B_2{}^T - \underset{\sim}{b}_1{}^T] \underset{\sim}{q}_1 + [b_3 + \underset{\sim}{b}_2{}^T V \Lambda^{-1} V^T \underset{\sim}{b}_2] \theta \; +$$

$$+ \; \underset{\sim}{b}_2{}^T V \int_o^t E_x(t-\tau)[V^T \beta_2{}^T - \Lambda^{-1} V^T B_2{}^T] \underset{\sim}{\dot{q}}_1 d\tau \; + \tag{63}$$

$$- \; \underset{\sim}{b}_2{}^T V \int_o^t E_x(t-\tau) \Lambda^{-1} V^T \underset{\sim}{b}_2 \dot{\theta} d\tau$$

Eqs. (62) and (63) can be compared with those resulting from the phenomenological approach, in this case eqs. 3.9 and 3.10 in Christensen [15]. Modifying his notation, to bring it in line with this development, we write:

$$\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_o = \int_o^t G(t-\tau,0) \underset{\sim}{\dot{q}}_1 d\tau - \int_o^t \underset{\sim}{\phi}(0,t-\tau) \dot{\theta} d\tau \tag{64a}$$

$$S - S_o = \int_o^t \underset{\sim}{\phi}{}^T(t-\tau,0) \underset{\sim}{\dot{q}}_1 d\tau + \int_o^t m(t-\tau,0) \dot{\theta} d\tau \tag{64b}$$

Taking the $\underset{\sim}{q}_1$ and $\theta$ terms in eqs. (62) and (63) under the integrals, we make the association:

$$G(t-\tau) = B_1 - B_2 V \Lambda^{-1} V^T B_2{}^T - [B_2 V - \beta_2 V \Lambda] E_x(t-\tau) \; \cdot$$

$$\cdot \; [V^T \beta_2{}^T - \Lambda^{-1} V^T B_2{}^T] + \frac{1}{2} T_o [\beta_1 - \beta_2 V V^T \beta_2{}^T] \delta(\tau-t) \tag{65a}$$

$$m(t-\tau) = b_3 + \underset{\sim}{b}_2{}^T V \Lambda^{-1} V^T \underset{\sim}{b}_2 - \underset{\sim}{b}_2{}^T V E_x(t-\tau) \Lambda^{-1} V^T \underset{\sim}{b}_2 \tag{65b}$$

$$\underset{\sim}{\phi}(0,t-\tau) = - \underset{\sim}{b}_1 + B_2 V \Lambda^{-1} V^T \underset{\sim}{b}_2 - B_2 V E_x(t-\tau) \Lambda^{-1} V^T \underset{\sim}{b}_2 \; +$$

$$+ \; \beta_2 V E_x(t-\tau) V^T \underset{\sim}{b}_2 \tag{65c}$$

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$$\phi^T(t-\tau,0) = - \underset{\sim}{b}_1{}^T + \underset{\sim}{b}_2{}^T V \Lambda^{-1} V^T B_2{}^T + \underset{\sim}{b}_2{}^T V E_x(t-\tau) \cdot$$

$$\cdot [V^T \beta_2{}^T - \Lambda^{-1} V^T B_2{}^T] \tag{65d}$$

It can now be seen from eqs. (65c&d) that $\phi(0,t) = \phi(t,0)$ ,
a symmetry property which is assumed in many works [15,29,32,33]
but apparently has not been proven previously.

Another interesting feature of the stress-strain law, eq. (62),
is the appearance of the $\dot{\underset{\sim}{q}}_1$ term outside the integrals. This term
represents the dependence of the stress state upon the instantaneous
strain rate, which is now seen to be a natural result of the second-
order approximations of entropy production and free enthalpy. The
term may be incorporated under the strain-rate history integral by
use of the Dirac delta function. This has been done in eq. (65a) to
facilitate comparison of eqs. (62) and (64a). It would seem advanta-
geous, however, to consider this term separately from the relaxation
modulus. Its presence precludes any instantaneous elastic response.
Since solid materials generally exhibit a measurable instantaneous
response, the coefficient of $\dot{\underset{\sim}{q}}_1$ is customarily taken to be zero.

Much of the derivation up to this point has been aimed at
deducing this symmetry of $\underset{\sim}{\phi}$ in its two arguments. With this accom-
plished, and with the machinery at hand, we address the question of
thermomechanical coupling.

Since most polymeric materials have poor thermal conductivity
and since small temperature changes are anticipated, it is reasonable
to model most transient deformation tests as adiabatic processes.

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This approximation reduces eq. (37) to $dS_I = dS$ , which we shall write as

$$\dot{S}_I = \dot{S} \tag{66}$$

From eqs. (48) and (54c), we then have:

$$\frac{1}{2}[\dot{q}_1^T \beta_1 \dot{q}_1 + 2\dot{q}_1^T \beta_2 \dot{q}_2 + \dot{q}_2^T \beta_3 \dot{q}_2] = b_3 \dot{\theta} - b_1^T \dot{q}_1 - b_2^T \dot{q}_2 \tag{67}$$

After application of eqs. (56b) and (57),

$$0 = \frac{1}{2}\dot{q}_1^T \beta_1 \dot{q}_1 + \dot{q}_1^T \beta_2 V\dot{q} + \frac{1}{2}\dot{q}^T \dot{q} - b_3 \dot{\theta} + b_1^T \dot{q}_1 + b_2^T V\dot{q} \tag{68}$$

After elimination of $\dot{q}$ , using eq. (58), and much cancellation of terms:

$$0 = - b_3 \dot{\theta} - \frac{2}{T_o} b_2^T VV^T b_2 \, \theta + [b_1^T - b_2^T VV^T \beta_2^T]\dot{q}_1 +$$

$$- \frac{2}{T_o} b_2^T VV^T B_2^T q_1 + \frac{4}{T_o^2} b_2^T VV^T B_2^T q_1 \theta + \frac{2}{T_o^2} b_2^T VV^T b_2 \theta^2 +$$

$$\tag{69}$$

$$+ \frac{2}{T_o^2} q_1^T B_2 \, VV^T B_2^T q_1 + \frac{1}{2}\dot{q}_1^T[\beta_1 - \beta_2 VV^T \beta_2^T]\dot{q}_1 - \frac{2}{T_o} b_2^T V\Lambda q +$$

$$+ \frac{4}{T_o^2} b_2^T V\Lambda q \theta + \frac{4}{T_o^2} q_1^T B_2 V\Lambda q + \frac{2}{T_o^2} q^T \Lambda^2 q$$

Eq. (60) is used to eliminate $q$ , giving:

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$$0 = - b_3\dot{\theta} + [\underset{\sim}{b}_1{}^T - \underset{\sim}{b}_2{}^T V V^T \beta_2{}^T]\,\dot{\underset{\sim}{q}}_1 + \tfrac{1}{2}\dot{\underset{\sim}{q}}_1{}^T[\beta_1 - \beta_2 V V^T \beta_2{}^T]\,\dot{\underset{\sim}{q}}_1 +$$

$$- \frac{2}{T_o}\underset{\sim}{b}_2{}^T V \int_0^t E_x(t-\tau)\left\{[V^T B_2{}^T - \Lambda V^T \beta_2{}^T]\dot{\underset{\sim}{q}}_1 + V^T\underset{\sim}{b}_2\dot{\theta}\right\}d\tau +$$

$$+ \frac{4}{T_o^2}\underset{\sim}{b}_2{}^T V \left[\int_0^t E_x(t-\tau)\,\dot{\theta}d\tau\right]\left[\int_0^t E_x(t-\tau)\left\{V^T B_2{}^T - \Lambda V^T \beta_2{}^T\right\}\dot{\underset{\sim}{q}}_1 d\tau\right] + \tag{70}$$

$$+ \frac{2}{T_o^2}\left[\int_0^t \dot{\underset{\sim}{q}}_1{}^T\left\{B_2 V - \beta_2 V \Lambda\right\}E_x(t-\tau)d\tau\right]\left[\int_0^t \Xi_x(t-\tau)\left\{V^T B_2{}^T +\right.\right.$$

$$\left.\left. - \Lambda V^T \beta_2{}^T\right\}\dot{\underset{\sim}{q}}_1 d\tau\right] + \frac{2}{T_o}\underset{\sim}{b}_2{}^T V\left[\int_0^t E_x(t-\tau)\dot{\theta}d\tau\right]^2 V^T\underset{\sim}{b}_2$$

Since eq. (70) must hold for arbitrarily small values of $\dot{\theta}$ and $\dot{\underset{\sim}{q}}_1$, the sum of the first-order terms must itself approach zero. Thus:

$$b_3\dot{\theta} + \frac{2}{T_o}\underset{\sim}{b}_2{}^T V \int_0^t E_x(t-\tau)V^T\underset{\sim}{b}_2\dot{\theta}(\tau)d\tau = [\underset{\sim}{b}_1{}^T - \underset{\sim}{b}_2{}^T V V^T \beta_2{}^T]\dot{\underset{\sim}{q}}_1 +$$

$$+ \frac{2}{T_o}\underset{\sim}{b}_2{}^T V \int_0^t E_x(t-\tau)[\Lambda V^T \beta_2{}^T - V^T B_2{}^T]\,\dot{\underset{\sim}{q}}_1(\tau)d\tau \tag{71}$$

Comparison of eq. (71) with eqs. (65b&c) shows that eq. (71) may be expressed as

$$\frac{d}{dt}\int_0^t m(t-\tau)\dot{\theta}(\tau)d\tau = -\frac{d}{dt}\int_0^t \underset{\sim}{\phi}^T(t-\tau)\,\dot{\underset{\sim}{q}}_1(\tau)d\tau \tag{72}$$

A similar result is derived by different means by Christensen [15].

Examination of eqs. (64) gives physical insight into the nature of the functions m and $\phi$. $\underset{\sim}{\phi}$, in eq. (64a), is the viscoelastic material function whose elastic analogue is the product of the volumetric coefficient of thermal expansion and the isothermal bulk modulus. In eq. (64b), m is the creep-type function corresponding to the heat capacity at constant volume in the elastic case. From the second law of thermodynamics, we see that this function must be non-decreasing. $\underset{\sim}{\phi}$ is harder to classify. The contribution of the thermal expansion will be a creep-type function, while the bulk modulus will be a relaxation-type function. Their product will be a hybrid of sorts, probably increasing for some short time and then slowly decreasing again.

While the heat capacity, thermal expansion, and bulk modulus have all been shown experimentally to exhibit time-dependent behavior, such effects are usually small and the functions can be sufficiently well approximated by step functions. Constant values for $C_V$, $\alpha$, and K are reported in most handbooks. Taking these constants to be appropriate asymptotic values, and noting that isotropy requires that $\underset{\sim}{\phi}$ take the form

$$\underset{\sim}{\phi} = - \alpha K(1,1,1,0,0,0)^T \tag{73}$$

(where the strain vector, $\underset{\sim}{q}_1$, is arranged in the usual fashion; the three shear components following the three normal components), eq. (72) can be simplified to:

$$\rho_o C_V \dot{\theta} = - \alpha K T_o \dot{\epsilon}_{kk} \tag{74}$$

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Equation (74) specifies the thermodynamic relationship between volumetric strain and the induced thermal change. It should be noted that a very important phenomenon, that of heating due to shear dissipation, is not accounted for in this formula. The contribution of shear deformation to thermal change has been lost in the linearization which entered the derivation in eqs. (54) and (71).

Heating due to shear deformation must be independent of the sense of shear when the deformation occurs from an unstrained state. Consequently, the dependence of $\dot{\theta}$ on $\dot{\underset{\sim}{\varepsilon}}$ must be an even function in each of the shear deformation components and cannot be included in a linear approximation.

To include this phenomenon in the present report would not only require retention of the quadratic terms currently present in eq. (70), but would also necessitate the introduction of cubic terms in the expansion of the Gibbs' free enthalpy (eq. (53)) so that quadratic terms would appear in the expression for entropy (eq. (54c)).

The ensuing analysis becomes quite involved and is not included in this report. Derivation of a phenomenological expression for heating due to shear dissipation remains a subject for future investigation.

CHAPTER FOUR

## COMPARISON AND SUMMARY

Although the derivations necessary to find the temperature change
due to deformation differ in a great many details between the infini-
tesimal elastic and viscoelastic cases, the results (eqs. (15) and (74))
are essentially identical. It remains to evaluate the material proper-
ties of significance, and to determine from them the extent to which
thermomechanical coupling effects need to be considered.

Since eq. (74) will be applied to small deformations of metals,
rubbers, and plastics alike, data are presented in Table Three for all
three classes of material. Calculations have been made for a temperature
of 25°C. $\Delta\varepsilon_{kk}$ is the volumetric strain necessary to induce a tempera-
ture change of one degree centrigrade. P is the hydrostatic pressure
necessary to cause that volumetric strain. $\varepsilon_{lin}$ is the longitudinal
strain associated with $\Delta\varepsilon_{kk}$ in a uniaxial tension test. Units used
in Table Three are: $\alpha$ , $10^{-5}/°C$ ; $\rho$ , $gram/cm^3$ ; E , K , $10^4 cal/cm^3$ ;
$C_V$ , $cal/gram/°C$ ; P , $10^4$ psi.

The volumetric strain associated with a one degree change in tem-
perature is seen to vary from about $0.1\%$ to 0.7% , with the polymeric
materials exhibiting much more diversity than the metals. The compres-
sive stress associated with this volume change varies from 500 to 4000
psi among the polymers, and from 700 to 5000 psi among the metals.

Also calculated is the strain that is necessary in uniaxial tension
to cause a temperature drop of one degree centigrade. The values for
metals are fairly consistant, ranging from 0.44% to 0.60%, with the

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TABLE 3.    TEMPERATURE CHANGE VS. VOLUMETRIC STRAIN[9]

| MATERIAL | $\alpha$ | K | E | $\rho_o$ | $C_V$ | $\frac{\alpha KT}{\rho_o C_V}$ | $\Delta\varepsilon_{kk}$ | P | $\varepsilon_{lin}$ |
|---|---|---|---|---|---|---|---|---|---|
| **METALS** | | | | | | | | | |
| Aluminum | 7.5 | 1.80 | 1.7 | 2.70 | .204 | 730. | .0014 | 1.5 | .0044 |
| Copper | 5.0 | 3.29 | 3.2 | 8.96 | .0893 | 610. | .0016 | 3.2 | .0050 |
| Iron | 3.1 | 3.34 | 4.4 | 7.39 | .107 | 390. | .0026 | 5.3 | .0060 |
| Lead | 8.7 | 1.10 | 0.40 | 11.35 | .0281 | 890. | .0011 | 0.73 | .0090 |
| Nickel | 3.9 | 4.49 | 5.1 | 8.90 | .105 | 560. | .0018 | 4.9 | .0048 |
| Silver | 5.7 | 2.48 | 1.9 | 10.5 | .0540 | 740. | .0013 | 2.0 | .0052 |
| Tin | 6.0 | 1.39 | 1.2 | 7.31 | .0523 | 650. | .0015 | 1.3 | .0054 |
| Zinc | 10.5 | 1.66 | 2.5 | 7.0 | .0851 | 870. | .0011 | 1.1 | .0022 |
| Steel | 3.5 | 3.6 | 4.5 | 7.9 | .118 | 400. | .0025 | 5.4 | .0059 |
| **RUBBERS** | | | | | | | | | |
| Polyisoprene (Hevea) | 67. | .047 | | .913 | .386 | 270. | .0038 | 0.11 | |
| Polyisoprene (Ebonite) | 19. | .10 | .072 | 1.17 | .322 | 150. | .0067 | 0.41 | .028 |
| P'butadiene-co-styrene | 53. | .060 | .11 | 1.15 | .314 | 260. | .0038 | 0.14 | .0063 |
| Neoprene | 60. | .050 | | 1.23 | .476 | 150. | .0066 | 0.20 | |
| **PLASTICS** | | | | | | | | | |
| Polystyrene | 23. | .072 | .079 | 1.05 | .28 | 170. | .0060 | 0.26 | .016 |
| Polyvinyl-chloride | 24. | .098 | | 1.41 | .24 | 210. | .0048 | 0.29 | |
| P'methyl Meth-acrylate | 27. | .096 | .099 | 1.17 | .31 | 210. | .0047 | 0.27 | .014 |
| Low density P'ethylene | (75.) | .079 | .024 | .91 | .25 | 780. | .0013 | 0.062 | .013 |
| High density P'ethylene | | .11 | | .96 | .21 | 1200. | .00082 | 0.055 | |
| Nylon 6 | 62. | .079 | | 1.1 | .26 | 510. | .0020 | 0.096 | |

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9   Data from [5], [9], [44] for metals; [7], sec. 6., for rubbers; and
    [8], tables 4.10, 5.3, and 9.3 for polymers.

exceptions of lead (0.90%) and zinc (0.22%). These two metals differ
primarily in their Poisson's ratios. It should be noted that $\epsilon_{lin}$
exceeds the elastic limit for most, if not all, the metals presented.
This does not imply that such strains are obtainable elastically; it
is merely a result of the choice of 1° C. as a benchmark. Since the
strain-temperature effect is linear, these values can be used in calcu-
lating the thermal effect of lesser strains.

Calculations were also made for those polymers for which values of
Young's modulus were found. These materials show more variation;
$\epsilon_{lin}$ ranging from 0.6% to almost 3% . The discussion concerning $\epsilon_{lin}$
for metals is applicable to the rubbers and plastics as well.

The thermomechanical coupling effect has been shown to be insignif-
icant in the infinitesimal transient deformation of solids in almost
all cases. It should be reiterated that eqs. (15), (26), and (74) can
be used to accurately predict these small thermal changes, allowing one
to decide, in light of the known thermal dependence of the mechanical
properties and the accuracy desired, if thermomechanical coupling effects
need be considered. It has been shown in earlier chapters that the
equivalent heat argument is wholly unsatisfactory for such purposes.

The insignificance of the thermomechanical coupling effect has also
been shown for the finite elastic deformation of rubbers. Finite, non-
linear deformations of metals and viscoelastic materials are not con-
sidered in this work.

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## ACKNOWLEDGEMENTS